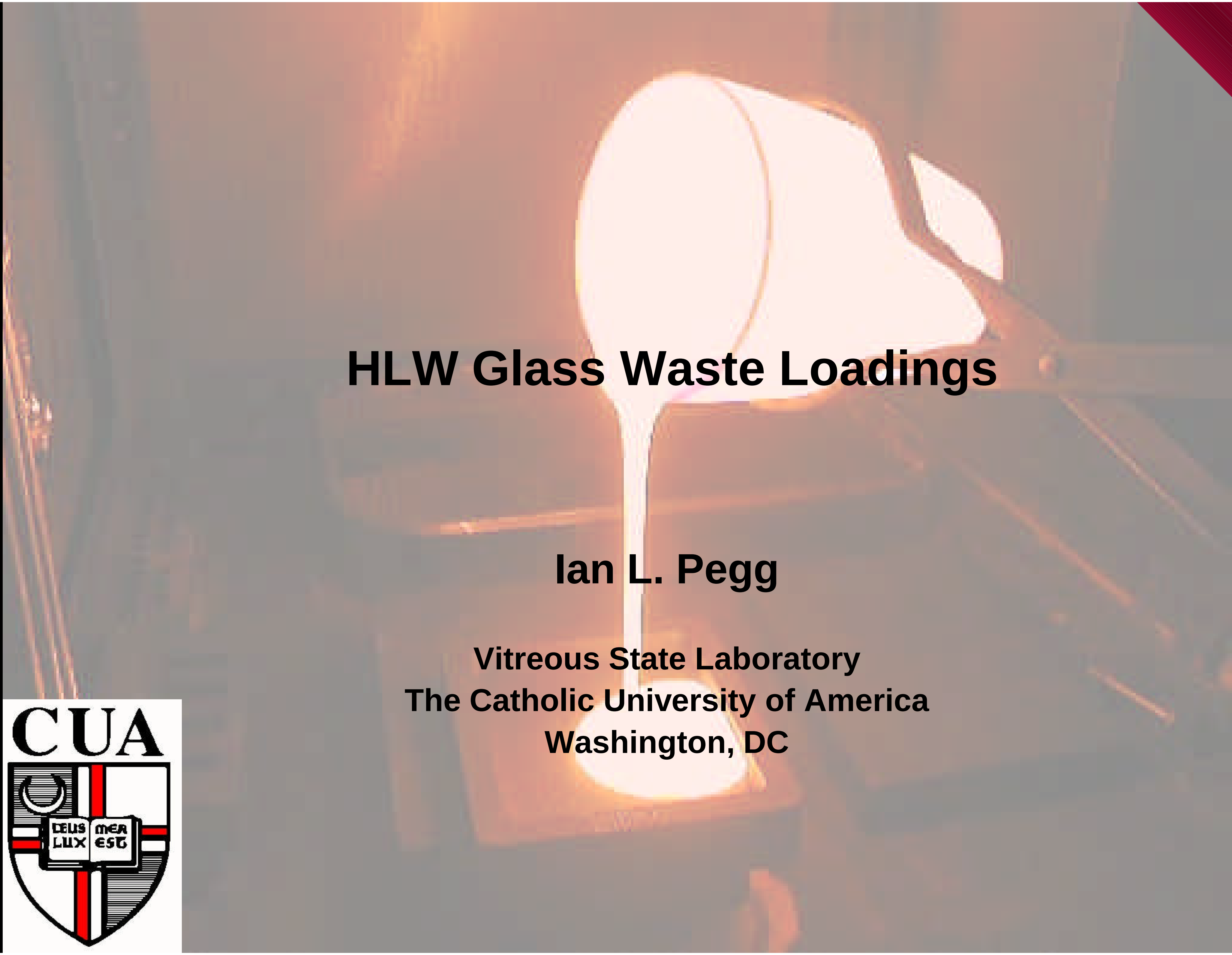

HLW Glass Waste Loadings

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Overview

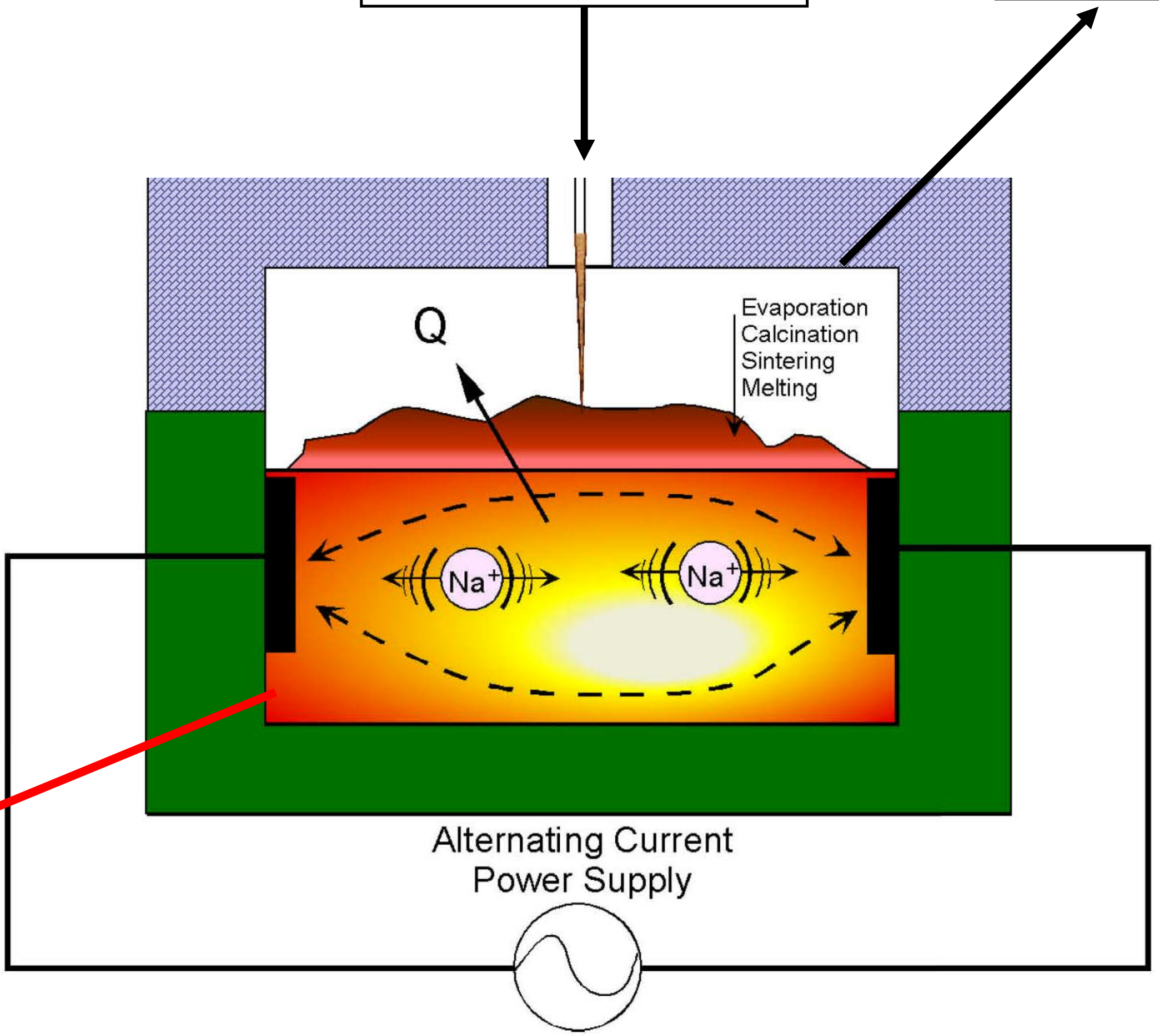
- Vitrification – general background
- Joule heated ceramic melter (JHCM) technology
- Factors affecting waste loadings
- Waste loading requirements and projections
    - WTP
    - DWPF
- Yucca Mountain License Application requirements on waste loading
- Summary

Vitrification

- Immobilization of waste by conversion into a glass
  - Internationally accepted treatment for HLW
- Why glass?
  - Amorphous material – able to incorporate a wide spectrum of elements over wide ranges of composition; resistant to radiation damage
  - Long-term durability – natural analogs
  - Relatively simple process – amenable to nuclearization at large scale
- There are numerous glass-forming systems – why *borosilicate* glass?
  - Relatively low-melting temperature
    - Materials of construction, component lifetimes
  - Potential for high chemical durability
  - ASTM C 162: “Borosilicate glass - any silicate glass having at least 5% of boron oxide (B_2O_3)”

JHCM – Principle of Operation

- Reaction at an interface so *melt rate* scales as the melt surface area, other things equal
- “Specific melt rate”
  kg/(m^2 d)
- Other factors also important (temperature, mixing, feed and glass composition, etc.)

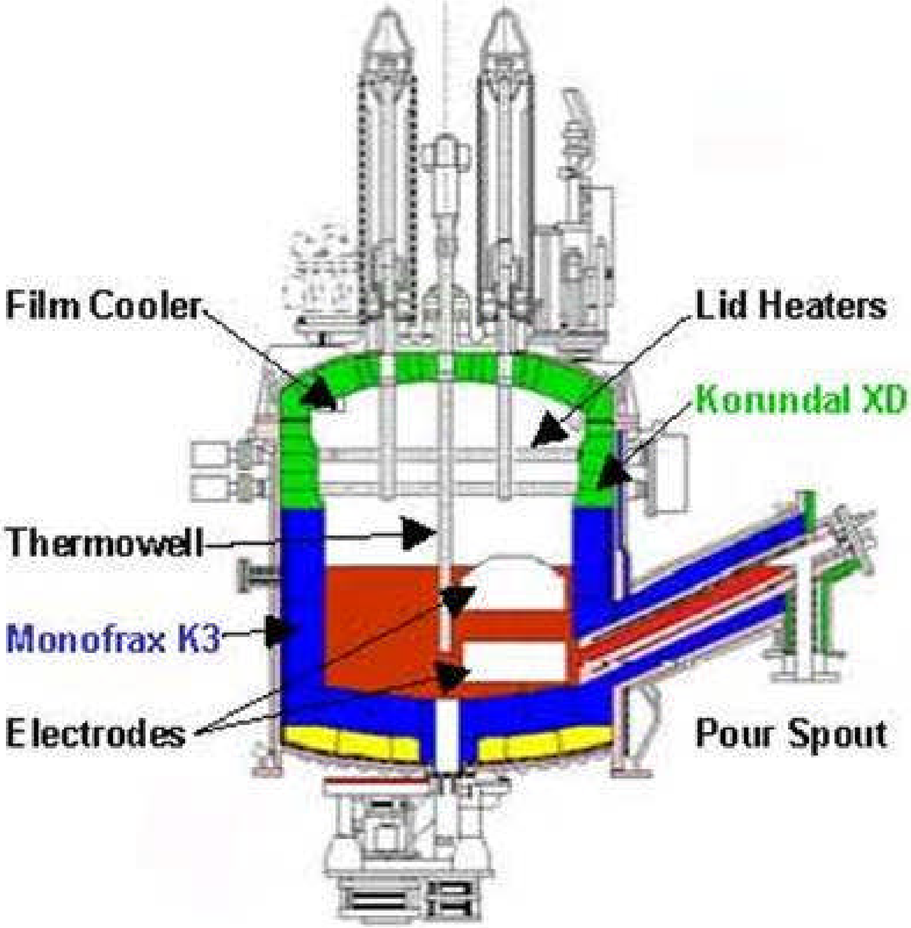


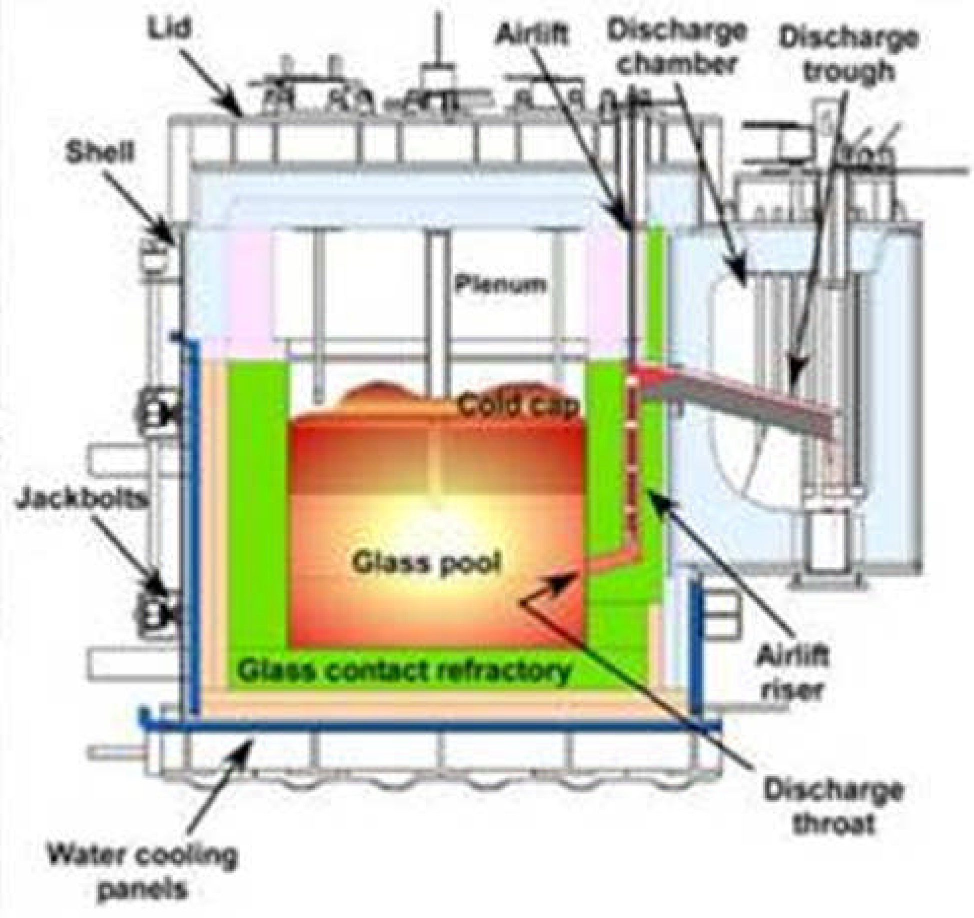
Waste + glass forming additives (chemicals or frit)

Off-gas

Glass Product

DWPF and WTP HLW Melters



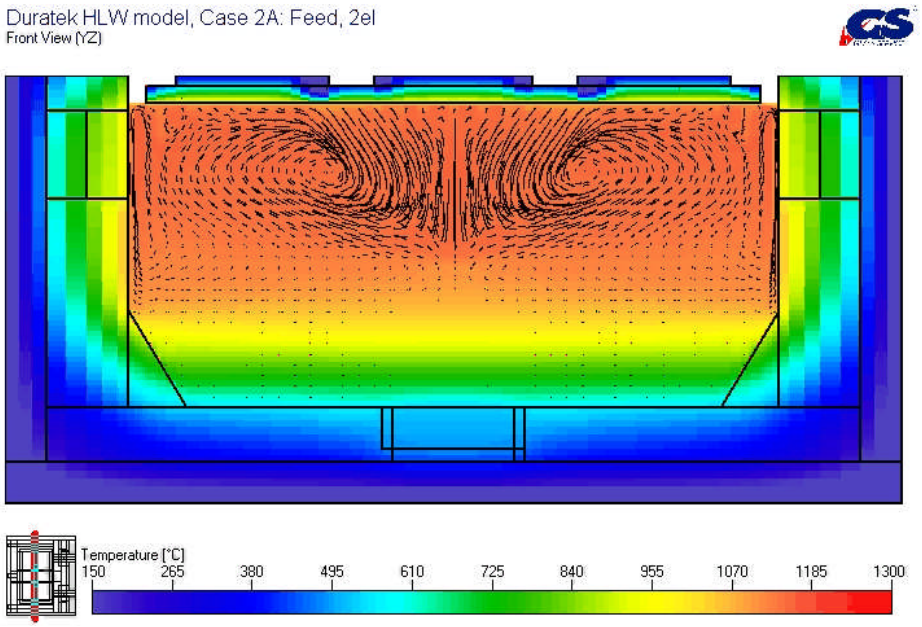


- 2.6 m^2 melt surface area
- Vacuum discharge
- Lid heaters
- Glass frit
- Bottom drain

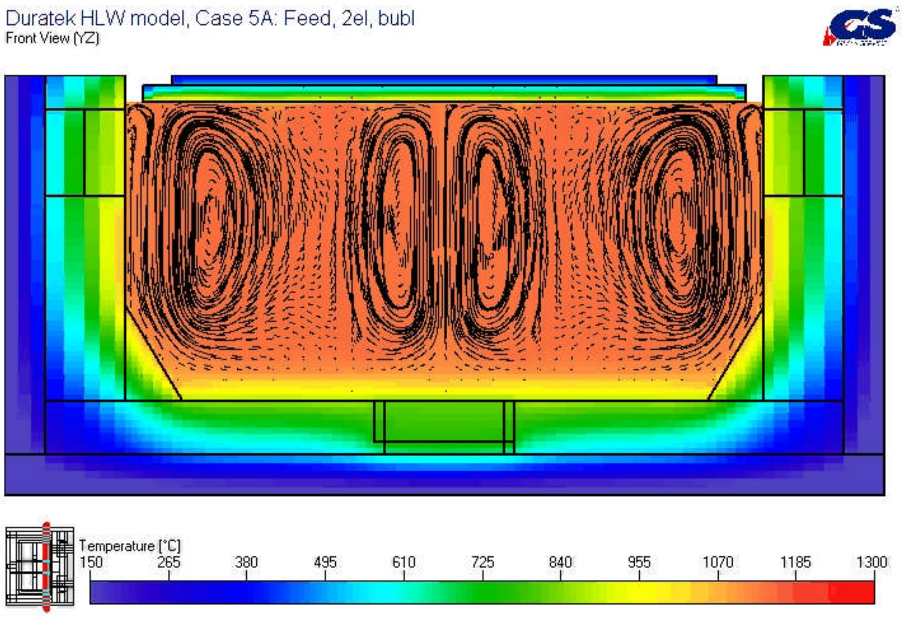
- 3.75 m^2 melt surface area
- Air-lift discharge
- Bubblers
- Glass forming chemicals
- WTP has two HLW melters

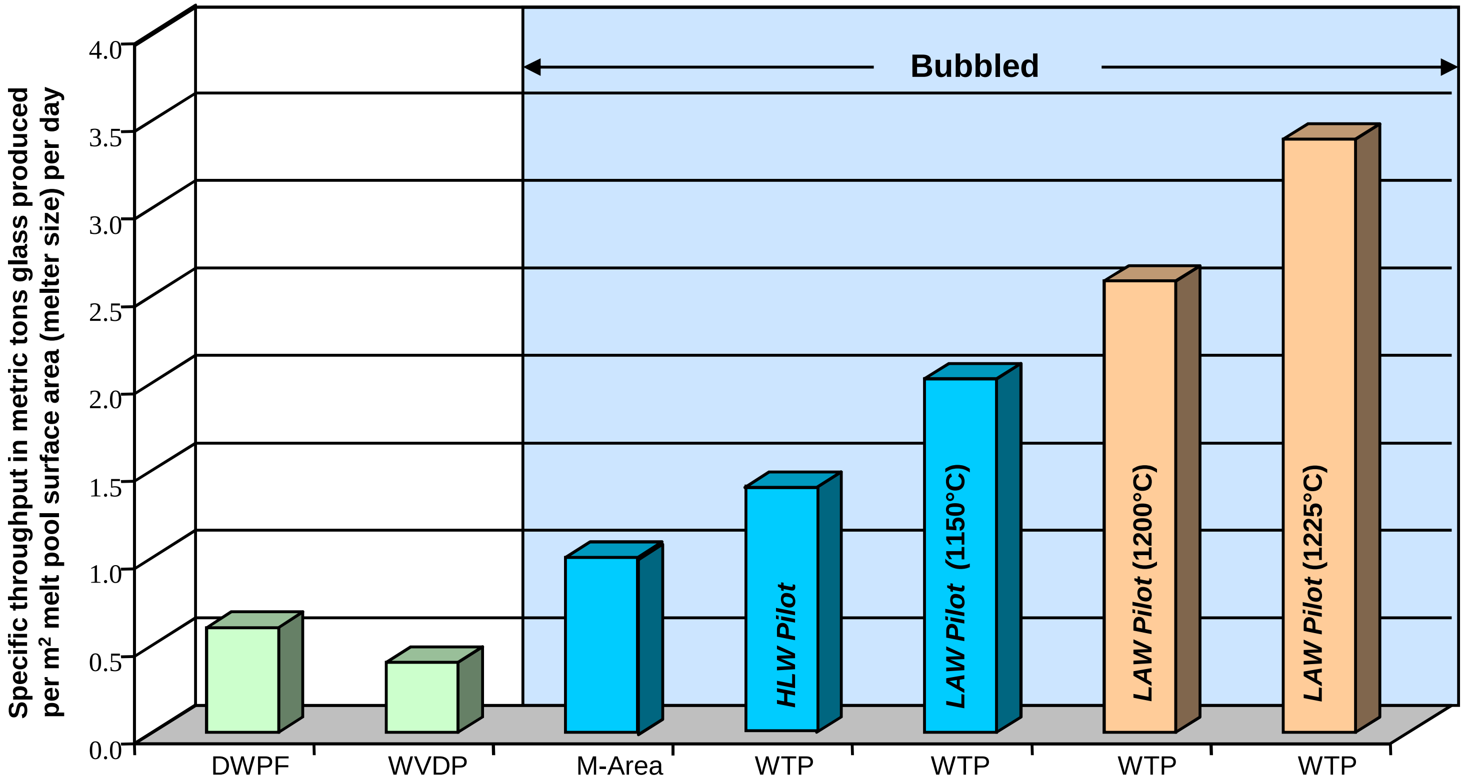
Effect of Bubbling

Unagitated JHCM
(West Valley, DWPF)



Agitated JHCM
(M-Area, WTP LAW, WTP HLW)





HLW Vitrification Enhancements

- Increased *waste loading* reduces canister count and increases waste treatment rate
  - Higher temperature, crystal management, enhanced glass formulations
- Increased *melt rate* increases waste treatment rate
  - Higher temperature, melt pool agitation (bubblers), enhanced glass formulations

Waste Treatment Rate = **Glass Production Rate** X **Waste Loading in Glass**

Primarily limited by crystallinity for HLW

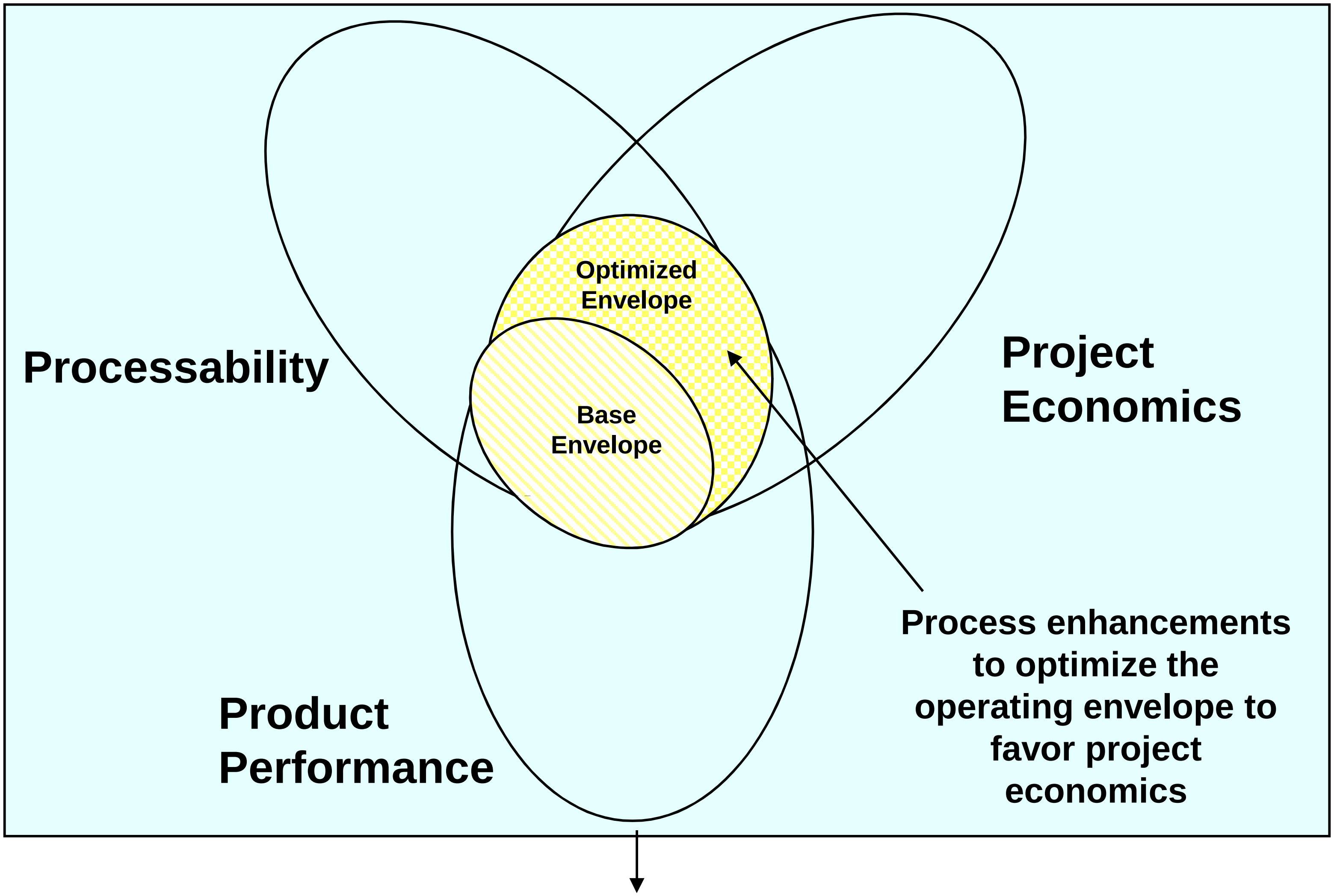
Crystallization in HLW Glasses

- Crystallization is the primary loading limiting factor for HLW
  - Processability – Melter tolerance to crystals and crystal management strategy (T_L vs. $T_{1\%}$)
  - Product quality – Nepheline formation for high-Al streams
    - Need for improved nepheline discriminator
- The limiting crystal phases typically incorporate several waste consitutuents
  - E.g., Spinels (Fe, Cr, Ni, Mn, Al, Mg…), nepheline (Al, Si, Na), other aluminosilicates (Al, Si, Na, K, Ca, Mg, Fe…), phosphates (P, Ca, Li…), etc.
- Limits are highly dependent on interactions between glass components, not simply single-component limits

HLW Vitrification Constraints

- Product quality
  - PCT
  - TCLP
  - TTT
  - Other regulatory constraints
- Processability
  - Melt viscosity
  - Melt electrical conductivity
  - Crystallinity
  - Processing rate
  - Salt formation
- Economic
  - Waste loading
  - Materials compatibility
- Other
  - E.g., feed rheology, flow-sheet decisions, etc.

HLW Vitrification Process Enhancements



Integration of glass of formulation with melter engineering is crucial.

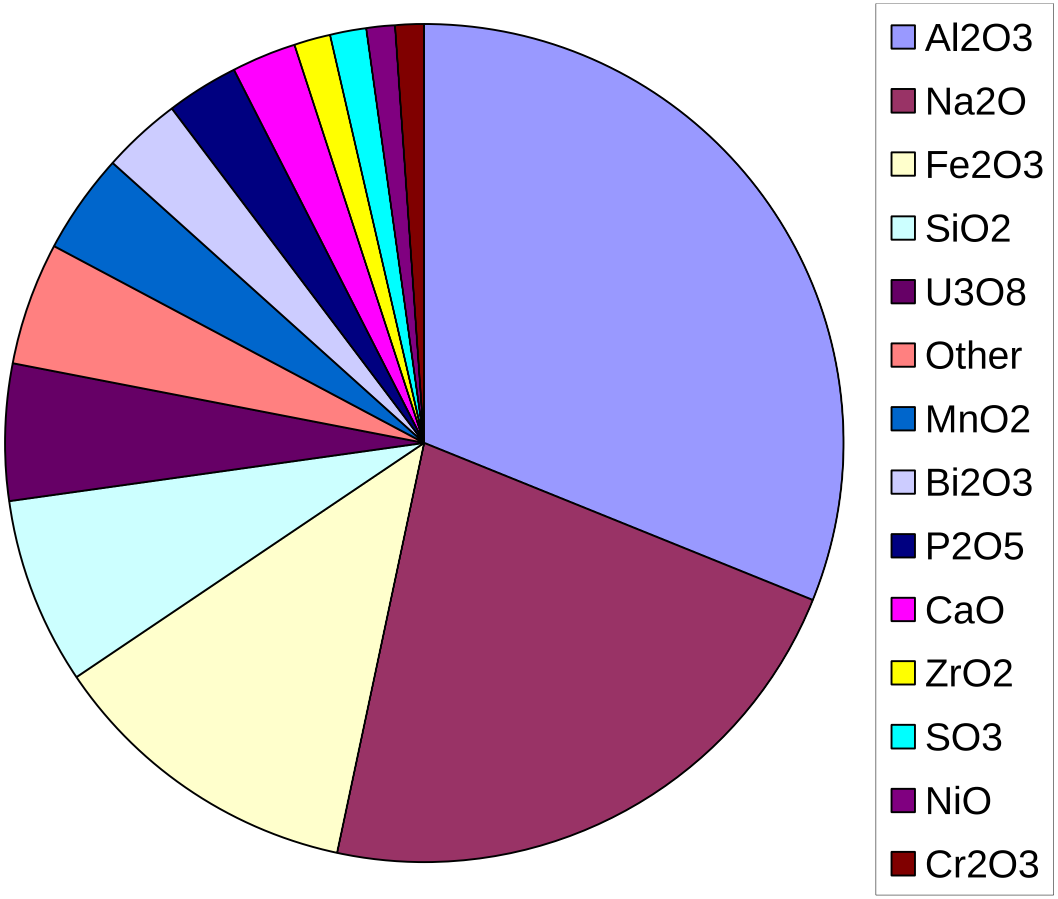
Component Effects on Glass Properties

- HLW glass properties are subject to various constraints
- All properties depend on glass composition
- As waste loadings are increased:
  - Glass composition changes
  - Glass properties change
  - Eventually one or more properties fall outside of acceptable limits
- These effects are captured in glass “property-composition” models – used for both projections and process control
- Models are limited by underlying data sets and assumptions
- Currently projected waste loadings reflect current state of models and available data
  - Improvements are possible

Feed Inventory to WTP HLW Vitrification

Per TF COUP Rev. 6

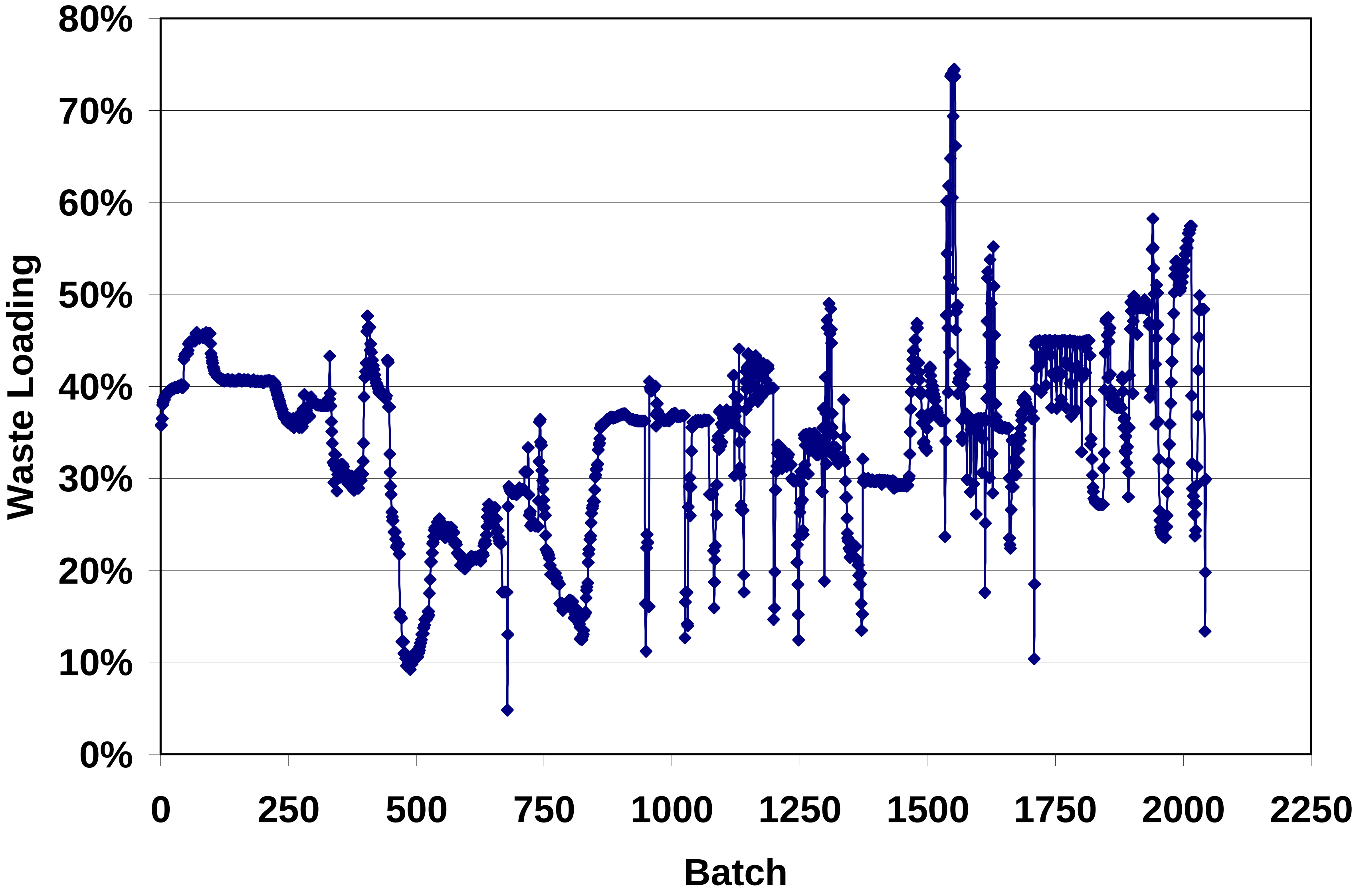
Waste Oxide	MT	%
Al2O3	3808	31.1%
Na2O	2729	22.3%
Fe2O3	1480	12.1%
SiO2	893	7.3%
U3O8	646	5.3%
Other	594	4.8%
MnO2	480	3.9%
Bi2O3	359	2.9%
P2O5	350	2.9%
CaO	301	2.5%
ZrO2	181	1.5%
SO3	159	1.3%
NiO	144	1.2%
Cr2O3	129	1.1%



- Compositions of individual batches vary greatly
- Projected overall average waste loading is 30 wt%
  - Range: 5 wt% (high SO_3) to 75 wt%
  - ~12,500 canisters

WTP Waste Loading Variations

Per TF COUP Rev. 6



WTP HLW Loading Requirements

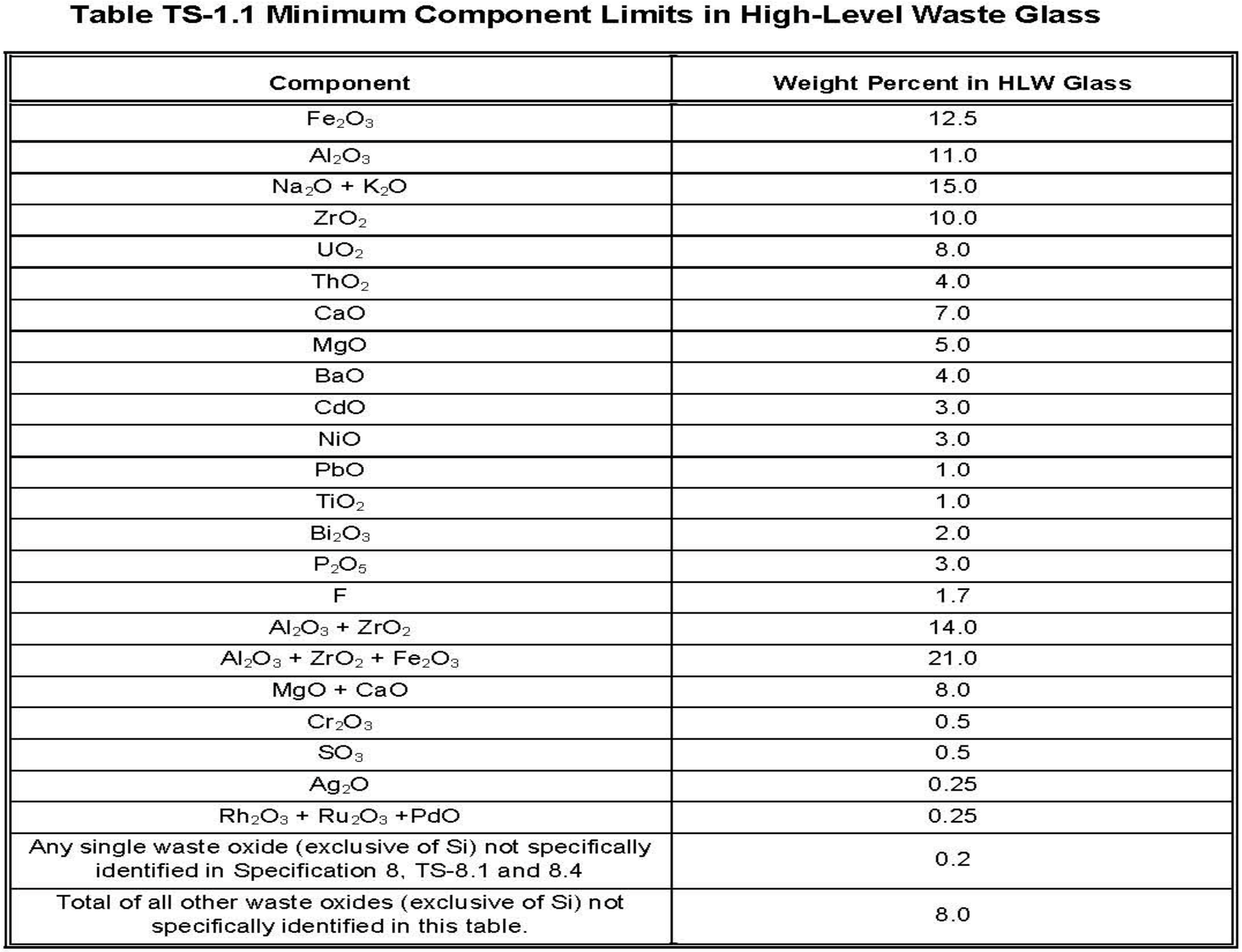


Table TS-1.1 Minimum Component Limits in High-Level Waste Glass

Component	Weight Percent in HLW Glass
Fe_2O_3	12.5
Al_2O_3	11.0
$Na_2O + K_2O$	15.0
ZrO_2	10.0
UO_2	8.0
ThO_2	4.0
CaO	7.0
MgO	5.0
BaO	4.0
CdO	3.0
NiO	3.0
PbO	1.0
TiO_2	1.0
Bi_2O_3	2.0
P_2O_5	3.0
F	1.7
$Al_2O_3 + ZrO_2$	14.0
$Al_2O_3 + ZrO_2 + Fe_2O_3$	21.0
MgO + CaO	8.0
Cr_2O_3	0.5
SO_3	0.5
Ag_2O	0.25
$Rh_2O_3 + Ru_2O_3 + PdO$	0.25
Any single waste oxide (exclusive of Si) not specifically identified in Specification 8, TS-8.1 and 8.4	0.2
Total of all other waste oxides (exclusive of Si) not specifically identified in this table.	8.0

Current WTP Model Validity Ranges

for Selected Components

HLW Glass Component	WTP Model Validity Range, wt%		WTP Contract Minimum
	TCLP	Other	
Al_2O_3	1.9 - 8.6	1.7 - 13	11
B_2O_3	4.8 - 14	4.4 - 15	None
Bi_2O_3	0 - 0.01	0 - 0.3	2
CdO	0 - 1.7	0 - 1.7	3
Cr_2O_3	0 - 0.5	0 - 0.6	0.5
Fe_2O_3	1.9 - 14	1.4 - 15	12.5
Na_2O	3.9 - 15	3.9 - 20	15 (Na_2O+K_2O)
NiO	0.1 - 1.0	0 - 1	3
P_2O_5	0 - 0.6	0 - 0.6	3
SiO_2	35 - 53	33 - 53	None
SO_3	0 - 0.2	0 - 0.33	0.5
ThO_2	0 - 6	0 - 6	4
ZrO_2	0 - 9.1	0 - 9.6	10

- Per contract, the focus of the BNI R&T effort has been on the first four HLW tanks
  - ~4% of the inventory, predominantly Fe-limited, none Al-limited
  - Well-developed but conservative baseline

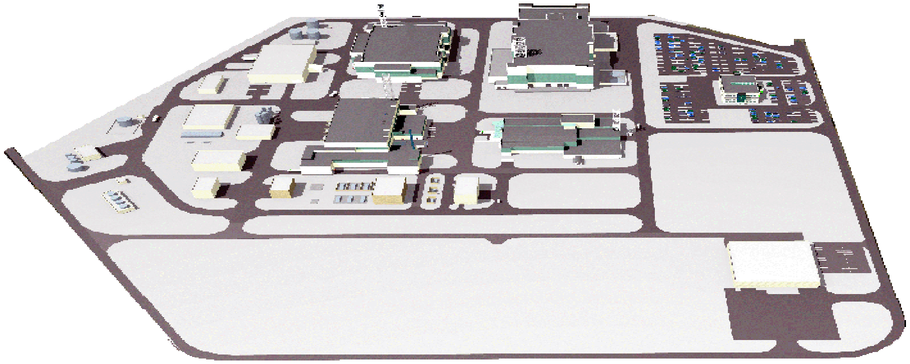
WTP High Aluminum HLW Streams

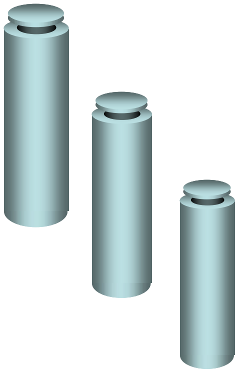
- Significant fraction of Hanford HLW streams are limited by Al
  - Nepheline is typically the primary limitation
  - Spinel is still a frequent secondary limitation
  - Spinel $T_{1\%}$ tends to increase with increasing Al
- Drives HLW canister count, mission duration, caustic leaching, Na additions, and LAW treatment capacity requirements
- Higher HLW glass loadings provides for system flexibility in trading off leaching in PT vs incorporation in HLW glass

Aluminum in WTP HLW

Based on TF COUP, Rev. 6

Hanford Tanks → WTP → Immobilized HLW Product





Al in Hanford Tanks:	Al in HLW Feed to WTP:	Al in WTP *Pretreated* HLW:
~ 8750 MT	~ 6200 MT	~ 2000 MT
Average Al_2O_3 loading in glass required to produce 12,000 canisters:	**~ 31 wt%**	**~ 10 wt%**

Peak loadings are much higher

Cumulative Distribution of Aluminum in WTP HLW Feed

TFCOUP, Rev 6

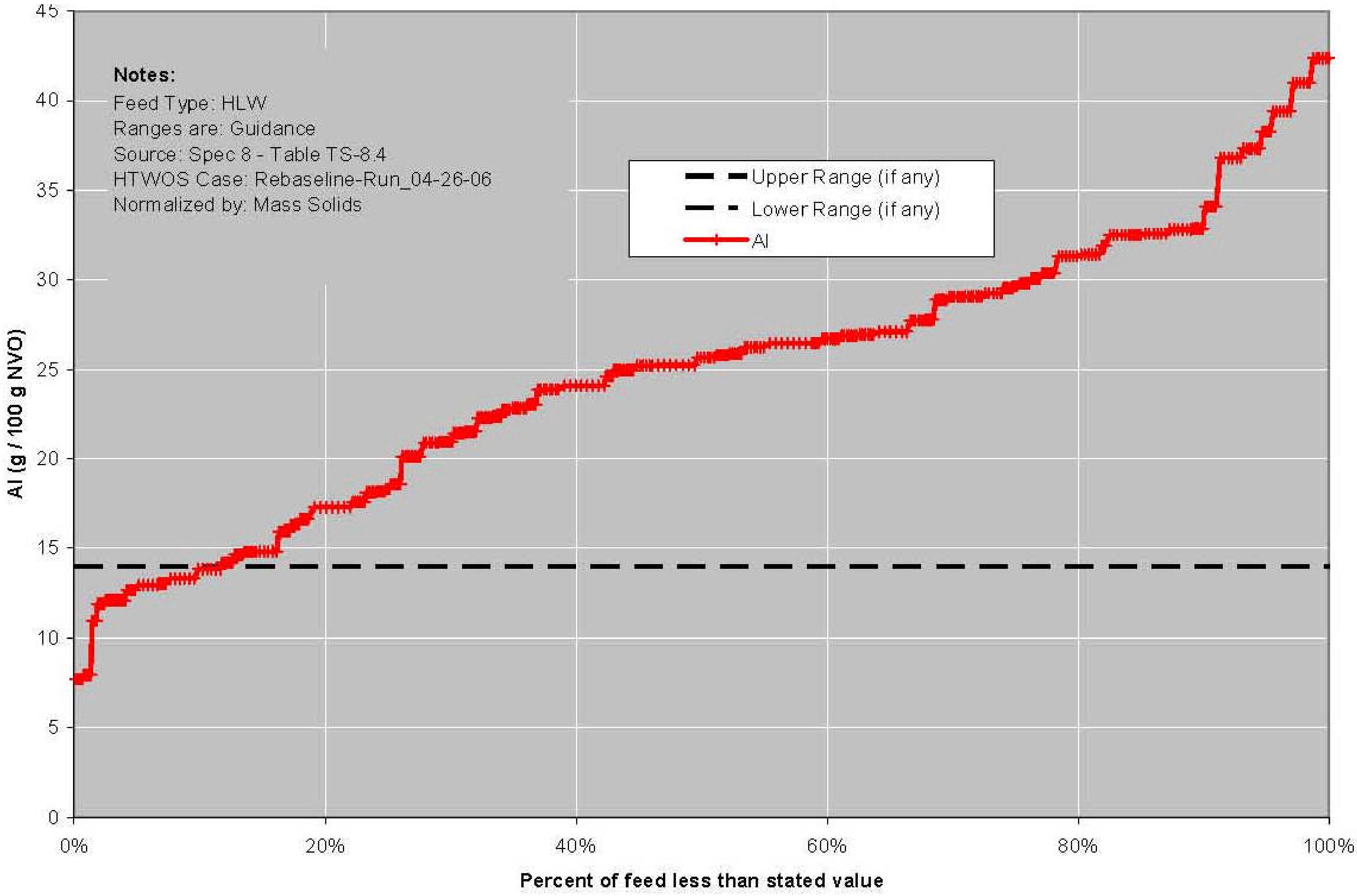
Wt% Al_2O_3

76%

57%

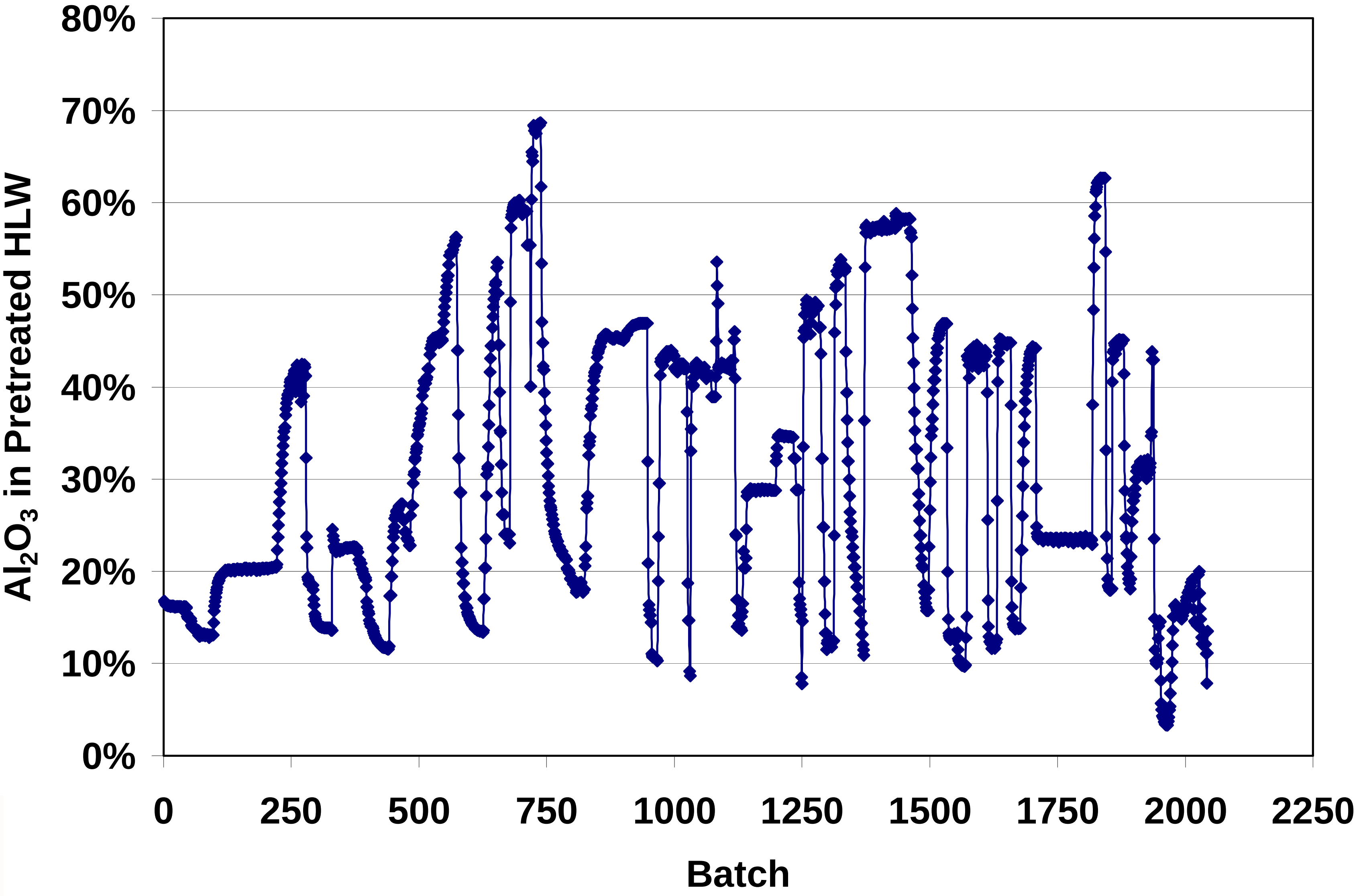
38%

19%



Notes:
Feed Type: HLW
Ranges are: Guidance
Source: Spec 8 - Table TS-8.4
HTWOS Case: Rebaseline-Run_04-26-06
Normalized by: Mass Solids

Alumina Content in WTP Pretreated HLW Feeds
Per TF COUP Rev. 6



WTP HLW Loading Enhancements

- Representative WTP balance-of-mission HLW compositions
  - Beyond BNI iron-limited early tanks
  - Waste types representing a larger fraction of the total inventory – limited by **Bi, Cr, Al, Al+Na**
- Glass formulation to determine maximum waste loadings
- Melter testing to assess processability, determine throughput, and obtain mass-balance information
- Identified and addressed low melt rates with high-Al loadings
- Modified feed and glass chemistry to increase melt rates while maintaining high waste loadings
- Validation in one-third scale HLW pilot melter runs

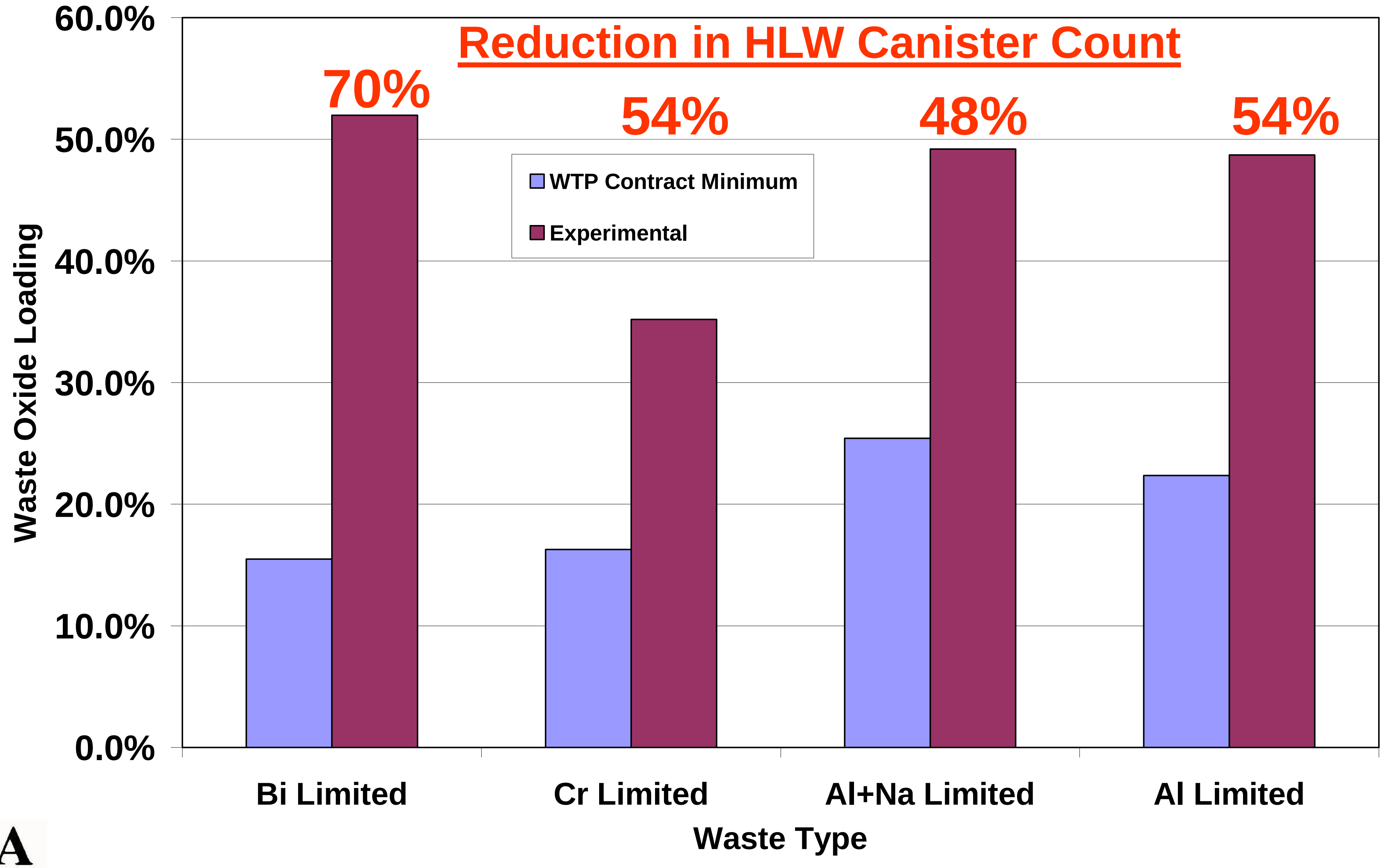
Source: VSL-08R1360-1, VSL-07R-1010-1

HLW Compositions Used

Waste Component	Bi Limited Waste	Cr Limited Waste	Al Limited Waste	Al and Na Limited Waste
Al_2O_3	22.45%	25.53%	49.21%	43.30%
B_2O_3	0.58%	0.53%	0.39%	0.74%
CaO	1.61%	2.47%	2.21%	1.47%
Fe_2O_3	13.40%	13.13%	12.11%	5.71%
Li_2O	0.31%	0.36%	0.35%	0.15%
MgO	0.82%	0.16%	0.24%	0.44%
Na_2O	12.97%	20.09%	7.35%	25.79%
SiO_2	12.04%	10.56%	10.05%	6.22%
TiO_2	0.30%	0.01%	0.02%	0.35%
ZnO	0.31%	0.25%	0.17%	0.36%
ZrO_2	0.40%	0.11%	0.81%	0.25%
SO_3	0.91%	1.52%	0.41%	0.44%
Bi_2O_3	12.91%	7.29%	2.35%	2.35%
ThO_2	0.25%	0.04%	0.37%	0.04%
Cr_2O_3	1.00%	3.07%	1.07%	1.44%
K_2O	0.89%	0.37%	0.29%	1.34%
U_3O_8	3.48%	7.59%	7.25%	4.58%
BaO	0.02%	0.03%	0.11%	0.06%
CdO	0.00%	0.01%	0.05%	0.02%
NiO	3.71%	1.06%	0.82%	0.20%
PbO	0.48%	0.48%	0.84%	0.18%
P_2O_5	9.60%	3.34%	2.16%	4.10%
F-	1.58%	2.00%	1.37%	0.46%
Total	100.00%	100.00%	100.00%	100.00%

Source: VSL-08R1360-1, VSL-07R-1010-1

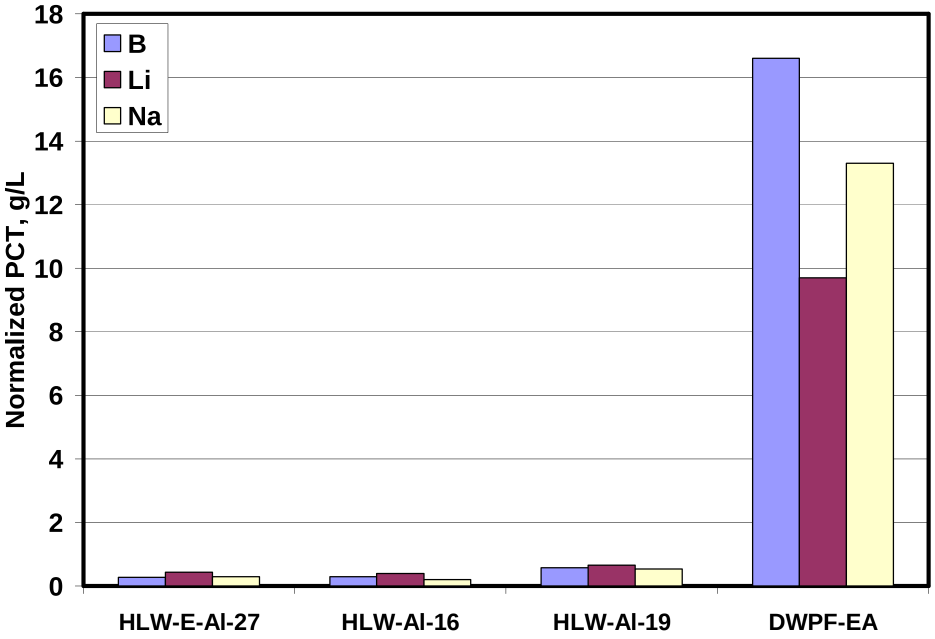
Waste Loading Summary



Source: VSL-08R1360-1, VSL-07R-1010-1

Melt Rate Improvement for WTP High-Al HLW Formulations

- Rapid melt rate screening tests and improved formulations developed
  - Confirmed increased melt rates in DM100 melter tests
  - Maintained 24 wt% Al_2O_3 loading
  - Meet all product requirements

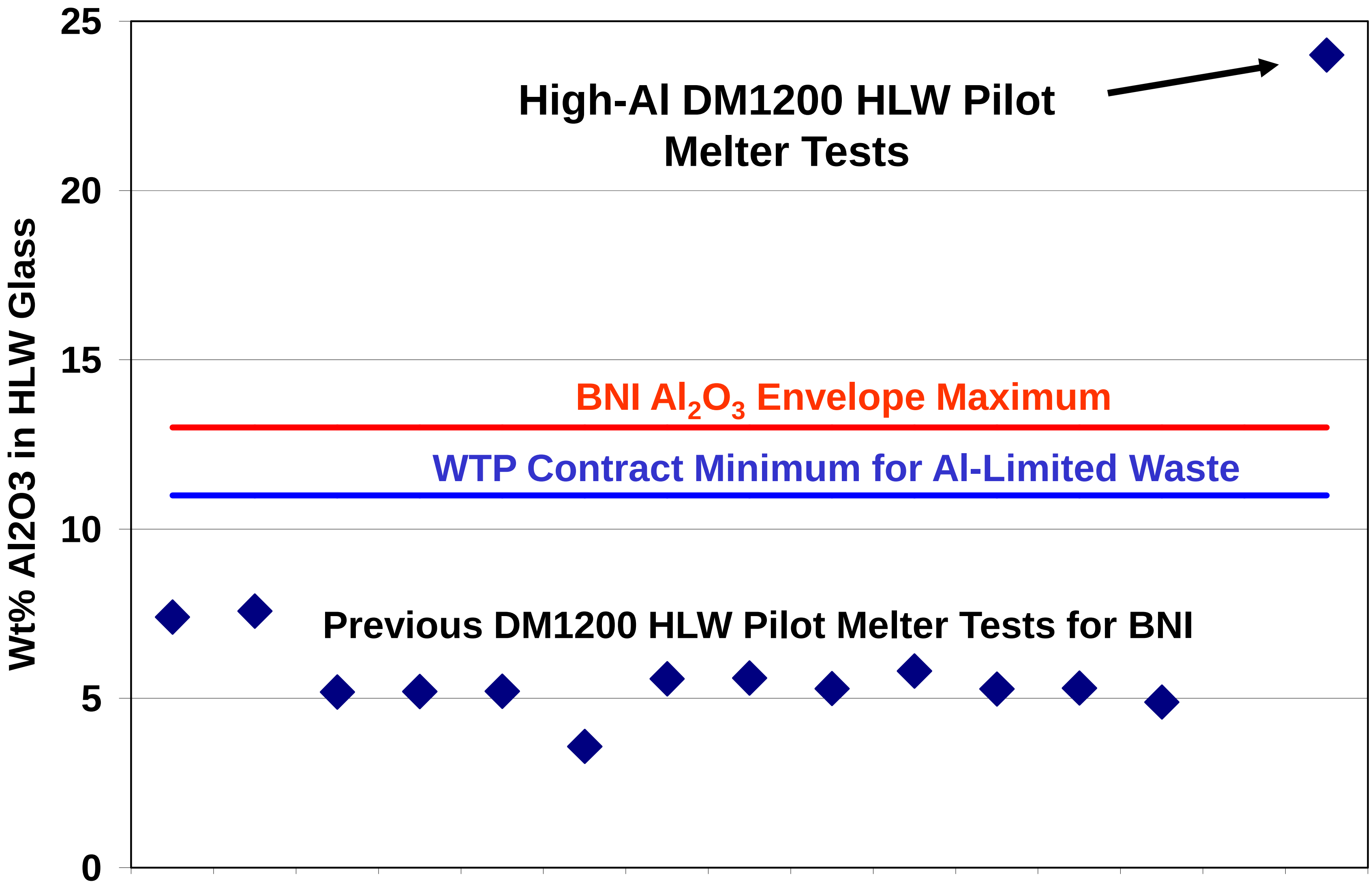


- Validated on DM1200 HLW Pilot Melter and integrated off-gas system
  - Test 1: 1150°C, 124 lpm bubbling 1500 kg/(m^2.d)
  - Test 2: 1150°C, 71 lpm bubbling 1050 kg/(m^2.d)
  - Test 3: 1175°C, 48 lpm bubbling 1050 kg/(m^2.d)

WTP Target: 800 kg/(m^2. d)

Source: VSL-08R1360-1, VSL-07R-1010-1

Alumina Content in DM1200 HLW Pilot Melter Runs



Source: VSL-08R-1010-1

Key Advances in JHCM HLW Vitrification Technology Facilitating Increased HLW Treatment Rates

CUA-VSL/ES Innovations Implemented at WTP

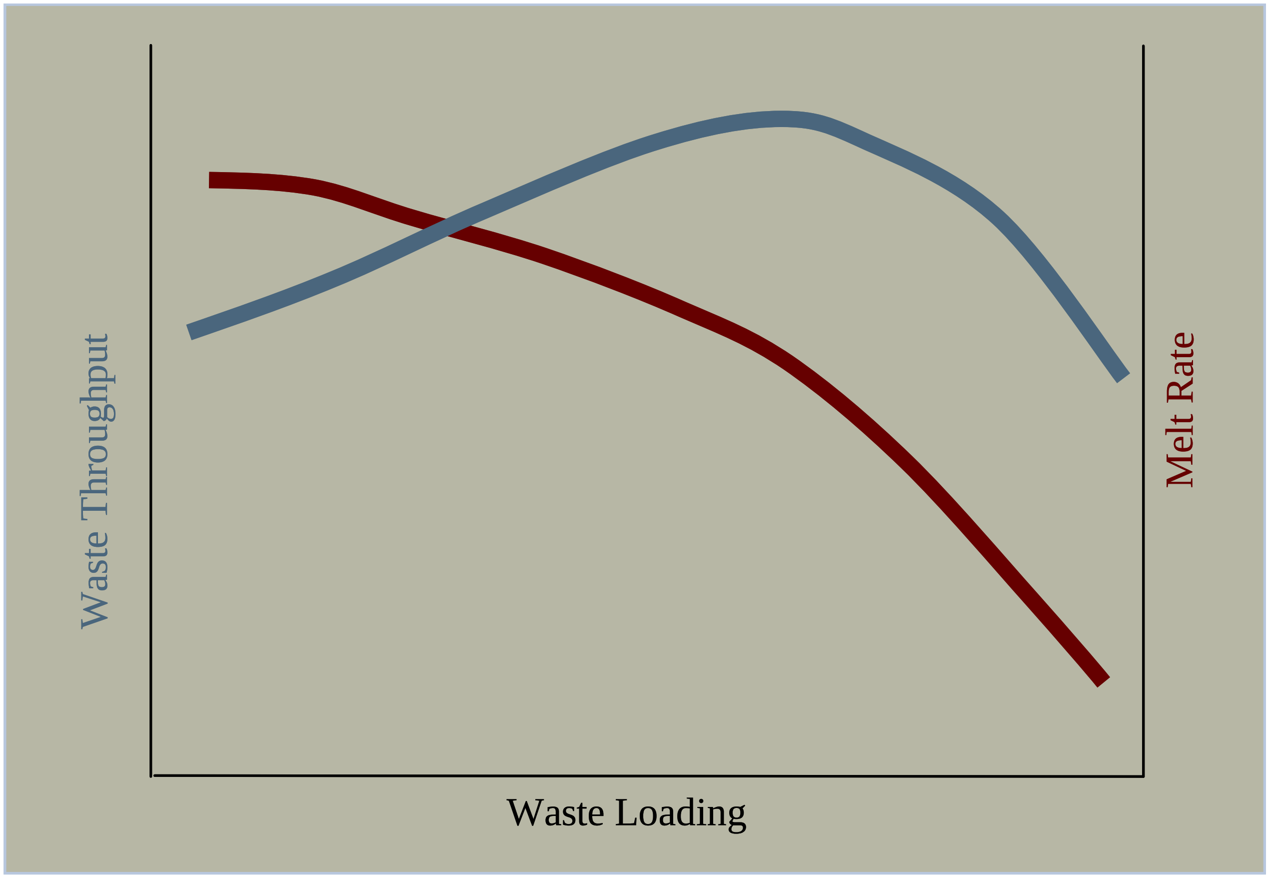
- Active melt pool agitation (bubblers)
  - Vastly increased melt rates
  - Improved temperature homogeneity allowing higher loadings
  - Improved crystal suspension allowing higher loadings
- Improved crystal management strategy ($T_{1\%}$ vs. T_L)
- Low silica glass formulations
- Improved glass property-composition models
- Potential for significant further improvements exist

DWPF Waste Loadings

- No specific waste loading requirement
- Initial operations targeted a minimum number of canisters produced per year
- Glass formulations employed “global” frit strategy
- Subsequent DOE incentives to increase waste loadings and melt rate led to the current tailored frit approach
- Waste loadings increased but decline of melt rates at high loadings was observed
- Therefore maximum waste treatment rates may be obtained at below the maximum achievable waste loadings
  - Trade-off: Waste treatment rate vs. canister count
- Need for melt rate screening tools identified

DWPF Waste Loading – Melt Rate Trends

Schematic



- Methods to offset or break this adverse relationship between melt rate and waste loading would be beneficial, e.g.
  - Active melt pool agitation (bubbling)
  - Improved glass formulations and property-composition models

<u>Source</u>: D. Peeler, EM-21 Workshop, 9/08

DWPF Waste Loadings

Date	Sludge Batch	Waste Loading	Waste Characteristics	Primary Constraints
1996 -1998	SB1	28%	High Fe (include simulated feed for startup operation)	-
Oct 98 - 2003	SB2	28% -34% (dependent on frits and throughput)	PUREX (High Fe Low Na)	-
Mar 04 - Apr 07	SB3	33% - 40% (dependent on frits and throughput)	PUREX (High Fe High Na)	TL
Aug 07 - Present	SB4	34%	H Modified (High Al Nominal 25%)	Nepheline, TL
Future (Begin Nov 08)	SB5	Target 36%	H Modified (High Al (21% w/dissolution), High Fe (>25%), High Na)	Nepheline, TL
Future (w/out Al-dissolution)	SB6-SB19	25%-41% (for operational flexibility) (Max 46%)	Al (19% - 34%)	Nepheline, TL, viscosity
Future (w/ Al-dissolution)	SB6-SB17	25%-41% (for operational flexibility) (Max 47%)	Al (12% - 23%)	Nepheline, TL, viscosity

Sources: WSRC-MS-99-00141; WSRC-STI-2007-00418; WSRC-STI-2007-00688;
J. Occhipinti, EM-21 Workshop, 9/08

DWPF Future Sludge Batches (SB6+)

Major Waste Oxides

Oxide	No Al Dissolution	With Al Dissolution
Al_2O_3	19 - 34 wt%	12 - 23 wt%
CaO	1.7 - 2.9 wt%	1.9 - 3.7 wt%
Fe_2O_3	19 - 34 wt%	25 - 41 wt%
MnO	1.2 - 8.9 wt%	2.1 - 11 wt%
Na_2O	19 - 28 wt%	20 - 22 wt%
NiO	0.2 - 3.9 wt%	0.3 - 4.5 wt%
SiO_2	2.5 - 8.3 wt%	1.8 - 7.3 wt%
ThO_2	0.0 - 1.8 wt%	0.0 - 3.1 wt%
U_3O_8	0.5 - 19 wt%	0.6 - 18 wt%

Source: SRNS-MS-2008-00068

Yucca Mountain License Application Requirements Potentially Relating to Waste Loading

Requirement	Notes
Waste Form	The standard vitrified HLW form shall be borosilicate glass sealed inside an austenitic stainless steel canister(s).
Durability of HLW Waste Form	Demonstrate control of waste form production by comparing production samples or process control knowledge to EA benchmark glass, using PCT or equivalent.
RCRA (Hazardous Waste Regulations)	The repository shall only accept HLW not subject to regulation as hazardous waste under the RCRA Subtitle C. Prior to acceptance for disposal, determine and document that RCRA-regulated wastes are not present. Hanford: Petitions for LDR variance and delisting established upper confidence intervals for RCRA components.
Phase Stability	Provide information on stability of vitrified HLW (TTT diagrams) and identify temperature limits needed to preserve waste form properties.
Thermal Output	Total heat generation rate for canisters containing HLW shall not exceed 1500 watts (5120 BTU/hr) per canister at time of shipment. The maximum temperature of vitrified galss shall not exceed 400C (Application 1.5.1.2.1.2.3). Hanford: 720 W/can (Application Table 1.5.1-19).
NWPA (Nuclear Waste Policy Act)	NWPA mandates a repository capacity limit of 70,000 MTHM (including 63,000 MTHM commercial SNF and 7,000 MTHM DOE SNF/HLW, divided as 2,333 MTHM for SNP and 4,667 MTHM for HLW). Various methods of calculating MTHM equivalence for HLW.
NWPA	The NRC has issued technical requirements and criteria (Part 60) for approving or disapproving DOE's application. E.g., radiation dose must be kept below regulatory limits of 100 mR per year for the general public and 5,000 mR per year for workers.
Criticality Potential in HLW Canisters	Provide qualified data to ensure wastes can demonstrate pre- and post-closure subcriticality. HLW canister criticality controls for normal operations and waste emplacement (pre-closure) are not necessary because of the low concentrations of fissile radionuclides in each canister (Application 1.5.1.2.1.2.4).
Information and Records	Radionuclide contents, organics contents, neutron/gamma dose rates, temperature history, product composition, method to assign MTHM equivalence …

Summary

- Achievable waste loadings are highly dependent on waste composition and vitrification system characteristics
- Crystallization is the primary loading limiting factor for HLW
  - Processability – Melter tolerance to crystals and crystal management strategy (T_L vs. $T_{1\%}$)
  - Product quality – Nepheline formation for high-Al streams
- Several features are common to both WTP and DWPF
  - e.g., high Fe, high Al leading to frequent spinel and nepheline limitations
- Considerably greater waste composition variability at Hanford leads to wider ranges of projected waste loadings
  - Limited data for many potentially limiting waste components
- Testing for some of the WTP balance of mission HLW compositions shows that waste loadings significantly higher than the WTP contract minima are possible
  - Fully compliant glass formulations with Al_2O_3 loadings up to 24 wt% demonstrated at 1/3-scale in HLW Pilot Melter runs with high melt rates
- "Tailored" vs. "global" frit strategy at DWPF has shown significant benefits
- Glass "property-composition" models used for both projections and process control are limited by quality of underlying data sets and assumptions
- Currently projected waste loadings reflect current state of models and available data; further improvements are possible